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Titanium Dioxide – A Missing Photo-Responsive Material for Solar-Driven Oil Spill Remediation

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Abstract

TiO₂ nanoparticles have been extensively investigated for environmental applications, particularly in the photocatalytic decomposition of organic pollutants using solar energy. The TiO₂-derived photocatalysts attract attention because of their photocatalytic efficiency and activity under a wide range of environmental conditions in response to superior structural and electronic properties. Consequently, TiO₂ compares with other common semiconductors used for environmental photocatalytic applications, TiO₂ is widely being considered close to an ideal semiconductor for photocatalysis. However, despite the impressive photocatalytic and material properties of titanium dioxide, TiO₂ has not to this point been incorporated within commercial hub of oil spill remediation products. Therefore, this chapter covers the description of inevitable technical details required for unveiling the full potential of solar-driven photooxidation potency of TiO₂, which have been the major challenges that halt its translation to commercial use in oil spill remediation. This at the end would underpin and make TiO₂-derived materials a substitute ready to be commercially accepted as a promising method for remediation of oil-polluted aquatic and soil environments.

Keywords: Photo-remediation, oil-spill, solar-radiation, pollution

1. Introduction

The aquatic and terrestrial environments are undergoing constant compositional change due to the continuous introduction of chemicals initiating pollution problems, which considered as part of the dominant threats to living systems surviving on the earth. Crude oil is a focal commodity upon which the economy of the world relies on and thus, its production is the largest and most profitable business in the world. This has, however, created burden and disturbances in ecosystems with attendant environmental quality imbalances. From its development phase to a production phase, many disasters occur in oil industries. An Oil spill is the most important type of disaster which usually occurs and causes a lot of environmental distress. Oil spill mishaps often happen during drilling, production, transportation, transfer, and storage [1]. Besides, the extensive utilisation of crude oil products and the discharges of oily wastewater have also caused increasingly serious oil spills pollution in the harbour and riverine areas as well as other water bodies [2, 3]. In effect, oil spills not only cause loss of energy source but also have long-term

damaging impacts on the ecological environment upon which our society relies [3–6]. And so, the negative impacts of oil spills to aquatic and terrestrial ecosystems can be significantly tremendous and unimaginable [7].

It is, therefore, in recent years, the problems of oil spills worldwide have attracted constant concern because of their ecological damage and environmental pollution. Oil spills in an aquatic environment is generally much more damaging since can spread to a distance of hundreds of miles in a thin oil slick layer covering the water surface. This eventually causes the chemical components and elements of the spilled oil to impact negatively on marine life, birds, photosynthesis in plants and as a result, disrupts the normal ecosystem services and structural food chain [1, 3, 4]. Similarly, oil spills pollution could also potentially impose disastrous effects on land [8]. The damage is hard to measure and contain since it involves complex ecosystems. Moreover, low-density spilled oils have an insufficient viscosity to pull together and can therefore speedily spread and damage unimaginable portions of land. On the other hand, high-density spilled oils are too viscous to be dispersed sufficiently well in the soil environment and thus, cause agglomeration that can give rise to stronger adhesive forces of attraction between oil and soil constituents. In either of the two scenarios, it may take land years to recover, during which spilled oils are able to destroy soils, its ecosystems, and biodiversity [9]. This is because oil contamination on land reduces plants' and the soil's ability to pull water from the ground and hold oxygen for plants' growth and micro-creatures survival, respectively. Thus, existing vegetation and fauna-diversity are prone to suffocation due to oil saturation and acts as a barrier, preventing water and oxygen getting to flora and micro-fauna, correspondingly [10]. Accordingly, transporting oil from production sources to consumption locations entails risks, most notably, the risk of accidental oil spills, which causes severe damage to ecosystems and loss to human society [11]. In addition, oil spill is a serious environmental problem not only because of its ability to pollute large areas with associated consequences, but also the longest period of management that usually leads to a heavy financial burden to industries and socio-economic afflictions to society in the immediate vicinity of the affected areas [12]. This is quite challenging because the consequences are not conditional upon the particular geographic, ecological and societal settings in which the disaster occurs, rather viewed as a global problem since crude oil is obviously traded inter-regionally and continentally [3, 11]. As such, the damaging impact and compositional alteration of the environment due to oil spills is one of the major concerns of today's world. For example, the tropical Gulf of Mexico oil spill reminds the world again of the importance of oil spill clean-up and environmental remediation [3]. Therefore, an efficient, economical and environmental friendly remedial action is urgently needed as a solution to oil spills pollution problems for the extermination of threats to plants, animals and human life on the gulf coasts and terrestrial environment.

Current remediation techniques for oil spills are typically classified as physical, biological, and chemical. These are the three primary remediation technologies that have widely been applied for addressing or decontamination of oil spills floating and/or dispersing in water and soil environments [13, 14]. The physical method has been considered as one of the most resourceful and inexpensive strategies for oil spills management [15], which is used to remove oil slicks from affected areas by functional materials. However, the process mainly involves the transfer of spilled oil from one environmental phase to another where disposal of oil-soaked agglomerates could also be another source or cause of environmental pollution. On the other hand, the biological method would have been the most attractive option, the hydrophobicity of weathered oil contributes to its low bioavailability to microbial actions, which increases the time for biodegradation and natural attenuation [16].

Although it can degrade oil without any recontamination [17, 18], but high-cost and a long period of action limit its practical application in emergency oil spill incidents that demand an economical and efficient approach [19]. The chemical method mostly involves the use of surfactants, dispersants, and solidifiers. Amongst the three, surfactants only break up oil into tiny droplets directing to help natural oil-eating microbes further break down the hydrocarbons. In contrast, dispersant perhaps do more harm than good. Dispersants hide the oil spills problem. It is used to accelerate the dispersion of the volume of oil into the water column, to reduce the visibility of oil pollution and of the potential impact on the biodiversity of the affected environment [20]. For the solidifiers, are mainly applied to immobilise oil to curtail further spread from concentrated and chunks of floating spilled oil on water or infiltrate into the soil when it occurs on the land surface. Unfortunately, solidified oil always requires to be removed and otherwise, the natural attenuation process of dispersion and volatilisation/evaporation will be inhibited leaving residues of solidified oil to be persistent due to slow weathering processes [13, 21].

It is believed that an oil spill spreads quickly and escalates rapidly and therefore, high speed of action is crucial. For this reason, the real short-time removal process of spilled oil from the environment, including water-bound systems, is imperatively needed for environmental sustainability. Although the application of TiO_2 in the clean-up of oil spills is a chemical method of environmental pollution remediation, in recent years, TiO_2 amongst the metal oxide semiconductors, has been considered as the most widely and well-studied material for the degradation of recalcitrant organic pollutants including spilled oil [22–24]. This is directly connected to its high photocatalytic efficiency, physicochemical stability, high photonic efficiency, and an absence of biological toxicity in bulk form. It also blends under a wide range of environmental conditions for its activity, including stability in acidic and basic aqueous media and activity under ambient temperatures, and most importantly widely available at low cost [25]. Despite these impressive photocatalytic and material properties, TiO_2 solar-driven remediation, as an *in-situ* self-remediation technique and a sustainable solution due to availability of the material and abundance of solar radiation, has not been fully developed. Moreover, it has not been, to this point, adequately incorporated within commercial oil spills remediation products. Thus, the question here that requires a wide spectrum of discursive clarification is that ‘will TiO_2 sunlight-driven photocatalytic remediation ever be fit for oil spills pollution tragedy in water and soil environments’? Or, is TiO_2 a missing material-based novel technique for solar-driven oil spill remediation?

Therefore, in this chapter, the properties of TiO_2 that whether or not make it fit to be considered as an ideal material for *in-situ* solar-driven photocatalytic remediation of oil spills, particularly in regions with high sunlight exposition and intensity, as well as the challenges that greatly restrict its application and the ability to translate and incorporate TiO_2 -containing materials to commercial use in oil spills remediation are discussed. This is aimed at providing research directions that can be skewed to work on facts rather than an impression in the design and development of TiO_2 -containing materials primarily for the solar-driven photocatalytic remediation of oil spills for environmental sustainability.

2. TiO_2 photocatalytic applications in environmental remediation

The potentials of applying photocatalysis in environmental management technology, particularly on pollution remediation, with prime focus on TiO_2 have been proven with spectacular results and reported in a number of research reviewed articles [12, 26–28]. The science of remediation involves removal, separation,

containment and destruction of pollutants or contaminants from host environmental media such as surface-and-ground water and soil. With respect to destruction, unlike the other remediation options that not only transfer pollutants from one medium to another, destruction converts contaminants to innocuous products, such as CO_2 and H_2O . In view of that, the photocatalytic destruction of contaminants in the environment, especially the application of irradiated TiO_2 -containing materials for the remediation of contaminants from environmental media has been applied successfully for a wide variety of compound [29, 30] such as alkanes, aliphatic alcohols, aliphatic carboxylic acids, alkenes, phenols, aromatic carboxylic acids, dyes, PCB's, simple aromatics, halogenated alkanes and alkenes, surfactants, and pesticides as well as for the reduction of heavy metals (Cr, U, As, Pb, Hg, Cd) from aqueous environments to soil surfaces [31–33]. In many cases, complete mineralisation of organic compounds has been reported [34, 35]. It is in records that in the overall field of semiconductor photocatalysis, both in fundamental research and practical environmental applications, TiO_2 has so far been shown to be the most promising material used for both circumstances because it is highly photo-reactive, cheap, non-toxic, chemically and biologically inert, and photo-stable [26, 27]. The major advantages of TiO_2 photocatalysis are that its process is not an energy-intensive pollution management method and is photo-responsive to renewable and pollution-free solar energy. Also, unlike the conventional environmental pollution treatment methods, TiO_2 photocatalysis does not transform parent pollutants to more refractory types, instead converts pollutants to innocuous products, such as CO_2 and H_2O . Besides, the reaction conditions are mild accompanied with modest reaction time and can be applied in gaseous, aqueous and solid phase pollution remediation techniques [30, 36–43]. Therefore, TiO_2 photocatalysis has the advantage of not only minimising pollution remediation project costs, but also resulted in the remediation reactions with the desired products in the most environmentally harmonious and safe ecologically.

The TiO_2 photocatalytic remediation processes exploits the high reactivity of oxygen superoxide ($\text{O}_2^{\bullet-}$) and hydroxyl (OH^\bullet) radicals as the oxidation driving forces resulting in the formation of benign by-products (i.e., H_2O and CO_2) of photo-mineralisation of toxic organic pollutants. Similarly, if a suitable scavenger or surface defect state is available to trap photogenerated electrons and holes and recombination is halted, a reductive pathway by a conduction-band electron(s) is also initiated. However, in very small TiO_2 nanoparticle suspensions both species are present on the surface. Therefore, simultaneous consideration of both the oxidative and the reductive pathways is required. In the remediation of organic pollutants of which spilled oil inclusive, TiO_2 utilises the oxidising power of the holes either directly or indirectly. On the other hand, to prevent a build-up of electrons, oxygen in the reaction environment serves as an electron acceptor that reacts with the electrons. The oxygen used in the process is atmospheric oxygen, and therefore, in general, there is no need for additional oxidising agents. Accordingly, TiO_2 has taken a highly prominent position of usage in solving environmental pollution problems both in aquatic and terrestrial environments. Similarly, it has taken centre stage in the campaign for solar-driven photocatalytic remediation of oil spills, as TiO_2 demonstrated the capability to develop such a green system that utilises renewal energy source and converts organic contaminants to innocuous products, such as CO_2 and H_2O that are environment friendly (**Figure 1**). From this perspective, as the most promising solar responsive semiconductor, TiO_2 -based materials are therefore expected to play a major role to curb serious environmental and pollution challenges through the utilisation of renewable solar energy. Therefore, oxidation of organic compounds by TiO_2 -based materials is of considerable interest

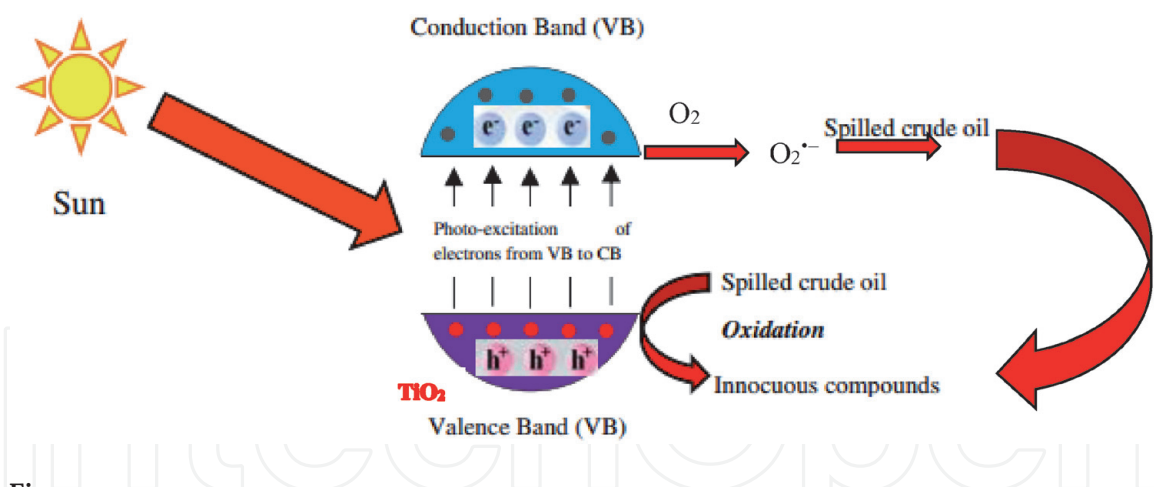


Figure 1.
 Photoremediation of spilled oil into innocuous compound by TiO₂ photocatalysis. (Sourced from Nyankson et al. [44] oil photocat itself) but modified.

for environmental applications, particularly for the control and eventual destruction or elimination of hazardous wastes such as spilled oils in aquatic and/or terrestrial environmental compartments. Accordingly, the oxidation process of TiO₂ is indiscriminate and therefore, leading to the mineralisation of almost all-organic pollutants in surface waters and soils.

3. Will TiO₂ photocatalytic remediation ever Be enough? The oil spills pollution tragedy in water and soil environments

The use of titanium dioxide (TiO₂) nanoparticles in oil spill remediation has not fully taken a positional value as a solution to oil pollution problem. The magnitude of being not considered for use in oil spill remediation remains on the impression that TiO₂ in powder form has a strong tendency to form much larger-sized aggregates or cluster and in most cases such agglomerations accounts for its reduced catalytic activity [45]. Another issue of concern involves separation and recovery of suspensions containing nanoparticles along with microparticles after use. These are some of the commercialisation-related challenges that impeding the acceptance of TiO₂ nanoparticles in oil spill remediation. This is enough to inspire scientists and engineers, particularly surface scientists and engineers around the world to become involved with fabrication and evaluation of TiO₂-containing materials for oil spill remediation, so as to make their functionality fully incorporated and suit with aquatic and terrestrial environmental requirements that will subsequently be translated to their commercial use in oil spill remediation. Currently, there has been limited information and engagements on the issue. In this context, because of impressive photocatalytic and material properties of TiO₂, fabrication of TiO₂-containing materials to commercial use in oil spill remediation need to be considered and given the desired attention due to the fact that oil spill pollution is one of the most disastrous infractions of environmental ethics.

Although TiO₂ has been demonstrated to have potential application in the fields of oil spill remediation with a number of advantages, however, the success of its application within the context of solar-driven technology is dependent upon definite factors encompasses of both material properties and environmental dynamic forces. On the material properties of TiO₂ nanoparticles, the issue of dispersion that leads to inevitable secondary pollution and low reusability; effect of aggregation; zero response to visible range of solar spectrum, which constituted its low efficiency

of the remediation process under visible light irradiation that greatly restricts its applications in surface waters and soils; wettability of a TiO_2 surface that depends upon the topography and the chemical composition of the surface; the problem of oil coagulation in aqueous environment and oil adsorption over TiO_2 largely depends on engineered surface chemistry of TiO_2 -containing material; and zero self-photochargeability. For TiO_2 to be incorporated within environmentally acceptable bulk material that can be translated to commercial use in oil spill remediation, intensity of light and the amount of oxygen available in the pollution-troubled environment; turbulence of water and wind current, which disturbs oil-material binding forces in surface water and soil environments must be considered. Therefore, if all these factors can be fully considered during the architectural and surface engineering design of TiO_2 -containing photocatalyst for oil spill remediation in surface waters and soils, TiO_2 -containing material would be considered as the most suitable candidate for oil spill remediation due to its impressive photocatalytic and material properties, as well as environmental suitability and compatibility. However, for discovery and initiation of a new brand of TiO_2 -containing photocatalyst for oil spill remediation under solar irradiation, the following need to be fully explored for the practical utility of this technique in commercial scale.

3.1 The problem of dispersion and aggregation of TiO_2 nanoparticles

On the issue of whether TiO_2 nanoparticles remains dispersed or forms much larger-sized aggregates or clusters that affect its photocatalytic activity in soil and surface water environments has already been documented and is strongly influenced by the ionic strength and pH of the aqueous suspensions in which TiO_2 nanoparticles is placed [46]. This clustering of TiO_2 nanoparticles is consistent with the principles of colloidal chemistry of other metal oxide nanoparticles, which rate of formation of nanoparticle aggregates in aqueous suspensions is a function of ionic strength and of the nature of the electrolyte in a moderately acid to circumneutral pH range typical of soil and surface water conditions [46–48]. It is true that clustering of TiO_2 nanoparticles has important repercussions for its practical uses in soils and surface waters. However, such problem can be overcome during architectural fabrication of nano-engineered surface of TiO_2 -containing material suitable for oil spill remediation by making sure that all the environmental parameters considered fall within ranges likely to be encountered in nature, specifically in situations where TiO_2 nanoparticles enters into contact with surface waters and soils. In another words, the wettability of the flat surface of TiO_2 -containing material can be engineered to assume the natural hydrophobicity of butterfly wings or lotus leaves, which forms solid-water or solid-soil solution static wetting mechanism that can enhance distribution by creation of evasion for the influence of ionic strength and pH of aqueous suspensions. With the intention to artificially make TiO_2 -containing photocatalyst as hydrophobic surfaces by introducing environmentally acceptable bulk material such as organo-clayed material to create roughness and reduced surface energy, the relationships between the water contact angle on a rough surface (θ_{rough}) and that on a flat surface (θ_{flat}) for homogeneous and heterogeneous wettings can be described by the Wenzel and the Cassie–Baxter equations, respectively. These two equations are shown as follows:

Wenzel's equation:

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{flat}} \quad (1)$$

Cassie–Baxter's equation:

$$\cos \theta_{\text{rough}} = \phi_s \cos \theta_{\text{flat}} - (1 - \phi_s) \quad (2)$$

where r is the roughness factor, defined as the ratio of the actual surface area to the geometrical one, and ϕ_s is the area fraction of the solid surface that comes into contact with water. Both the theories pointed out that a rough surface is essential for enhancing hydrophobicity and they are commonly used to explain the wetting behaviour on rough hydrophobic surfaces.

In addition, the wettability behaviour that occurs at the interface of the solid, air, water and oil can also be described on the value of the contact angle alone, where surface properties are usually categorised as hydrophilic, hydrophobic and superhydrophobic. If the water contact angle (θ) is less than 90° , the surface is described as hydrophilic, if θ is between 90° and 150° then hydrophobic and if θ is above 150° , the surface is described as superhydrophobic. The water contact angle (CA) θ is usually used to measure the wettability of a flat surface of the nanocomposites, which will depend on the solid–vapour, solid–liquid, and liquid–vapour surface tensions, and can be expressed by Young’s equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (3)$$

where γ_{SV} , γ_{SL} and γ_{LV} are the interfacial tensions between solid and vapour, solid and liquid, and liquid and vapour, respectively, as shown in **Figure 2**.

Such material modifications may be of particular importance in saline environments where high ionic strength could promote coagulation and precipitation of dispersed TiO_2 . In a positive note, for example, TiO_2 photocatalysts modified with hydrophobic coatings remain dispersed within organic target pollutants and do not lose photo-degradation efficiency after salt addition [49]. Hence, this result can help to delineate such potential limitation for *in-situ* application of TiO_2 nanoparticles in oil spill remediation, and can also provide insight to guide future material development effort in relation to controlling the buoyancy, hydrophobicity and other desired surface properties of TiO_2 -containing photocatalyst to enable oxidative radicals generation in proximity to floatable hydrophobic compounds such as oil spills.

Another difficulty that perhaps has not given TiO_2 edge in oil spill remediation involves separation and recovery of suspensions containing nanoparticles and/or microparticles after use, which leading to inevitable secondary pollution and low reusability. To address this problem, immobilisation of TiO_2 on a support material would render nanoparticles recovery unnecessary. Besides, immobilisation of TiO_2 unto a support is thus an advantage because it allows reusability of material in a number recycles. Therefore, for oil spill photo-remediation in surface waters, fabrication of a floatable photocatalytic material by immobilising TiO_2 on

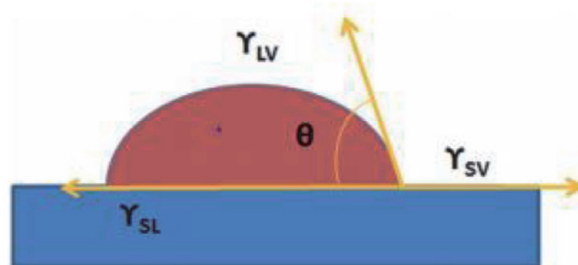


Figure 2.
 The interfacial tensions between solid and vapour, solid and liquid, and liquid and vapour.

environmentally acceptable bulk material can serve as a relevant brand of solution to the problem. For example, a floatable photocatalytic material by immobilising TiO_2 on expanded perlite, a siliceous rock of volcanic origin was fabricated and reported [50]. Similarly, TiO_2 nanotube films was successfully anchored on the surfaces of levees for use in degradation of low-level oil spills, e.g., oil spills in harbours [51]. A floatable TiO_2 -containing photocatalyst can not only maximise the illumination/light utilisation process, especially in a system with solar irradiation, but could also maximise addition of oxygen (oxygenation) to the photocatalytic system by the proximity with the air/water interface, especially for non-stirred reactions [51]. Accordingly, proximity of TiO_2 -containing material with the air/water interface can result in high concentrations of surface oxygen molecules to act as the primary electron acceptor, which can therefore trap electrons resulting in prevention of recombination of the electron-hole pairs and increasing the rate of electron scavenging by O_2 resulting in the formation of an increased yield of superoxide radicals ($\text{O}_2^{\bullet-}$) that can directly or indirectly contribute to the degradation and mineralisation of spilled oils. This can increase the rate of oxidation of spilled oil during photo-remediation, as floatable TiO_2 -containing photocatalyst can have the ability to interact with floating oil. The potential benefit of engineering of the surface of TiO_2 -containing photocatalyst that is sufficiently buoyant to maintain close proximity with floating oil and highly hydrophobic to act at the oil-water interface is to facilitate interaction with the powerful oxidative radicals generated in the process. Therefore, such proximity can be an advantage against low quantum efficiency due to the low rate of electron transfer to oxygen resulting in a high recombination of the photogenerated electron-hole pairs.

3.2 The problem of visible-light response of TiO_2

The use of TiO_2 in remediation of oil spills is sufficient enough because of its impressive photocatalytic and material properties, but one of the major technical challenges that restrict its large-scale application and its use in oil spill remediation technologies is that TiO_2 has a relatively wide bandgap (~ 3.2 eV, which falls in the UV range of the solar spectrum), and therefore it is unable to harness visible light thus ruling out sunlight as the energy source of its photo activation [52–55]. Because TiO_2 nanoparticles are only responsive to UV light of the solar spectrum, it means could only convert or utilise less than 5% of the total solar radiation (**Figure 3**), which is quite a small proportion of the solar spectrum. On the other hand, the solar spectrum that is mainly composed of about 95% visible light does not have enough energy to excite TiO_2 to be photocatalytically active (**Figure 4**). In view of that, one of the major challenges that hold the throat of scientists, government and entrepreneurial organisations is the development of material(s) using “clean and renewable” energy applications based on the sounding calls and/or demands of Green and Sustainable Science, to relieve the environmental burden due to pollution. In the quest to improve the photocatalysis ability of TiO_2 by responding to visible light or solar, several attempts have been made and shown that visible light responsive modified- TiO_2 based materials for environmental applications are sufficiently promising. Significant progresses have been made in the synthesis of novel materials and nano-structures of TiO_2 meant for efficient processes for the degradation of pollutants, particularly organics. As such, photocatalysis of TiO_2 can be considered as a well understood field of study; yet, immense challenges and opportunities exist in realising this technology for large scale practical applications in the decontamination of the environment, particular in relation to oil spill remediation [57]. Fortunately, fabrication of photo-active TiO_2 in a wide range of solar spectrum plus coating turns its engineered surface into a new smart and environmentally resilient

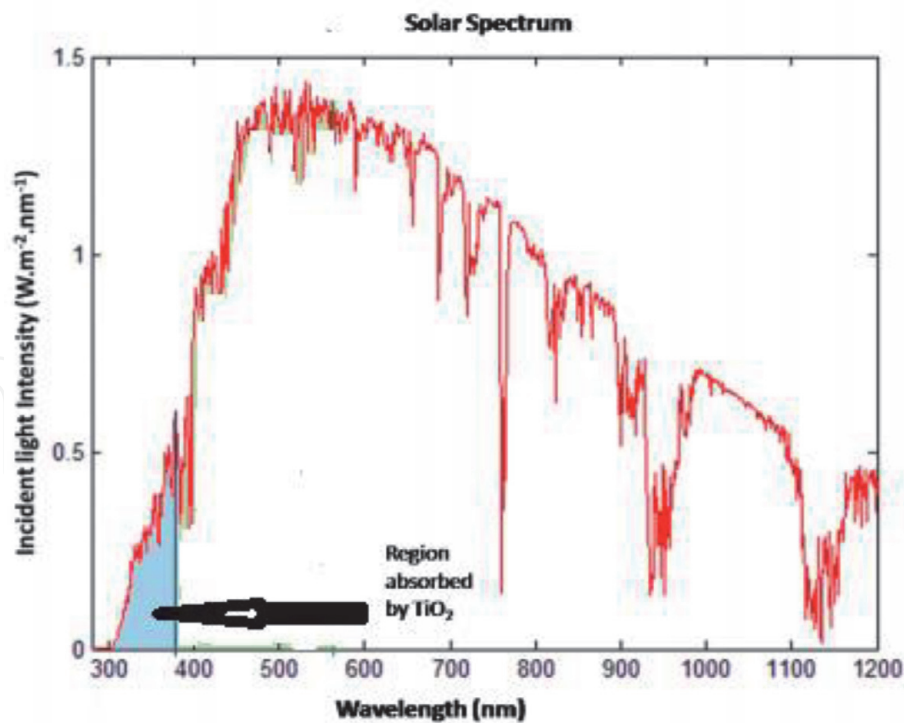


Figure 3.
Absorption region of TiO₂ in solar spectrum.

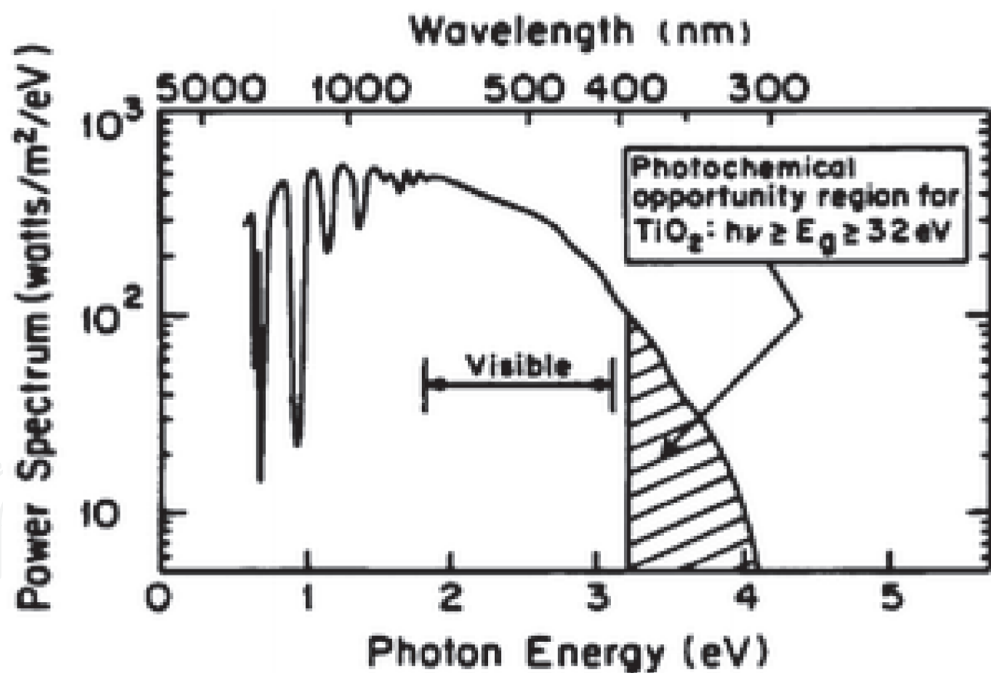


Figure 4.
Absorption of solar spectrum against bang gap of TiO₂. Sourced from Linsebigler et al. [56].

material that once exposed to solar light will be able to function well for the designated purpose.

Undoubtedly, TiO₂ is an efficient photocatalyst in the UV region, which corresponding to an absorption threshold of 390 nm. This restrains its utilisation in the visible range (400–800 nm) for practical applications using solar radiation as the light source. Therefore, for it to be use for oil spill clean-up whose prominent superiority is *in-situ* remediation under visible light irradiation, the surface of the material must be re-engineered. The technological application of TiO₂

photocatalysis in oil spills remediation processes require the development of TiO_2 -containing materials that are efficiently responsive to sunlight, since sunlight is the only free source of photons that can yield the desirable clean-up of huge volume of oil spills in a bearable cost. On the account that greater part of the solar radiation that reaches Earth is comprised of visible light couple with a minute fraction of ultraviolet radiation, several improvements have been made to overcome the limitation of solar spectrum to initiate photoexcitation over TiO_2 and optical responsiveness to the visible light region after modification has been reported feasibly [58–61]. Accordingly, it becomes apparent that with such ground-breaking discoveries, TiO_2 is a suitable and an excellent candidate for oil spills remediation and that in addition can pave ways and increase interest for its incorporation within commercial oil spill remediation products in coming years, because of this unique and superior optical property.

Another issue of concern that also limits all day(s) of full application of TiO_2 in oil spills remediation is one major drawback associated to all the traditional photocatalysts like TiO_2 that they can only work under illumination. Surface chemistry and engineering has provided a solution to this limitation, where visible-light-driven energy storage photo-responsive TiO_2 -containing photocatalysts have been developed and have been widely used in photocatalysis in dark in recent years [62–72]. Upon advancement, energy storage photocatalysts that are full-sunlight-driven made up of UV–visible–NIR with possession of long-lasting energy storage ability have also been advanced technologically. The materials exhibit a strong absorption at full-sunlight spectrum (300–1,000 nm) that cut-across UV–visible–NIR with a super-long energy storage time. In a system like this, the material system is composed of two kinds of composite materials [65, 71], namely light harvesting material and energy storage material. The light harvesting material is the material capable of absorbing light to generate electron–hole pairs while the energy storage material is the material in charge of trapping and saving the electrons or holes transferred from light harvesting centres during illumination, and releasing them in dark. In the architectural design of such new materials, hydrogen-treated (because hydrogen treatment can extend the light absorption threshold of TiO_2 to NIR) [73] and bulk surface modified- TiO_2 functions as the light harvesting material and also serves as a candidate in charge of the electrons or holes generation simultaneously, while a co-catalyst such Na_xMoO_3 is mainly made to display self-photochargeability effect by trapping and saving electrons [74]. The extraordinary full-spectrum absorption effect and long persistent energy storage ability make such material a potential solar-energy storage and an effective photocatalyst in practice, as such the material has dual functions by harnessing solar energy to excite electrons, store electrons and when light is over in a time there is no sunlight can still do the remediation reaction by allowing the stored electrons to go back to the photocatalyst and initiate the generation of oxygen superoxide radicals ($\text{O}_2^{\bullet-}$) for the degradation and mineralisation of pollutants under treatment. The oil molecules adsorbed over the surface or in the pores of TiO_2 -containing photocatalyst can be directly oxidised by the $\text{O}_2^{\bullet-}$ during the night operational process. The possible reaction pathways could be presented as shown below in Eqs. (4) and (5). The participation of crucial active species of $\text{O}_2^{\bullet-}$ in the photocatalytic remediation of diesel oil was detected under visible light illumination [75]. Accordingly, the non-stopped generation and the intensity of $\text{O}_2^{\bullet-}$ species in the remediation environment, it simultaneously expands the photocatalytic capacity of TiO_2 -containing photocatalyst with the increase of time. It means that long-time illumination can further enhance the photocatalytic remediation effect both in the day time and night. Therefore, the drawback of TiO_2 -containing photocatalysts that they can only function under illumination has been overcome and the long persistent energy

storage ability of the photocatalysts allows not only be used during daytime, but also be used during the night. Consequently, TiO₂-containing photocatalyst endowed with this new optical and electronic properties still presents TiO₂ as a missing material for its potential application using solar energy utilisation for oil spills remediation in all day(s) operational process.



In addition to above, to further enhance the solar-driven activity of TiO₂, up-conversion luminescence agent was coupled with TiO₂ to transform the unused near-infrared (NIR) sunlight tail into UV-vis radiation available for photoreaction activation and the result demonstrated promising contribution suggesting that it can be used for treating surface water and soil pollution problems using solar light [74]. This is an alternative approach of enhancing solar absorption ability of TiO₂ and the process is of considerable interest for photocatalytic processes because it produces UV-visible range from infrared light sources through multi-photon and energy transfer mechanisms. In the up-conversion photonic processes, materials such as rare-earth (RE) doped materials appear as one of the most promising candidates for efficient up-conversion luminescence that assist in the long-wavelength light harvesting of solar irradiation [76–78]. In fact, this technological advancement has already been applied in agricultural production by improving the sunlight conversion efficiency of the photosynthetic process. For that reason, when applied in TiO₂ photocatalysis, transforming the incoming infrared light into UV-visible light provides extra photons for absorption by TiO₂ and therefore, the process cannot only optimise TiO₂ photocatalytic remediation process, but also the incident radiation can lead to an endless range of possibilities. Interestingly, amongst the possibilities is that the process improves the photocatalytic activity of TiO₂ even when solar radiation intensity is low. Although the solar irradiance to be received by a body of water or soil in a particular location depends on its position in the Earth. The locations on the equator of the Earth receive solar radiation at a higher intensity (irradiance) than the norther and southern hemispheres (Figure 5). This means that more solar radiation reaches the surface at these altitudes. In other words, all locations receives visible light in the same wavelengths, but the brightness and intensity are very different. However, with a system of TiO₂

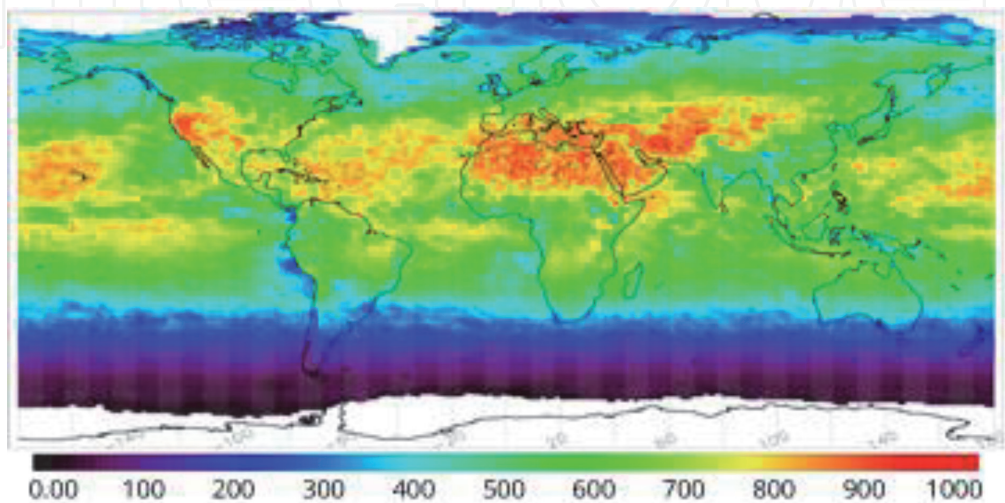


Figure 5.
Surface solar irradiance receives by different locations of the earth. Sourced from Wang et al. [79].

comprised of up-conversion luminescence agent, the problem of solar intensity in different locations of the Earth would no longer be an issue of challenge. This means that the perceived disadvantage of the location of the North and South poles with smaller solar exposition than the equator when it comes to application of photoremediation is now a false impression. Besides, the process also decreases the irradiation time needed for decontamination by solar light. As a result, when such technological process is applied in oil spills remediation, the rare-earth doped materials amalgamated with TiO_2 would facilitate increased solar absorption and higher energy conversion efficiency. This serves as a clear testimony that oil spills remediation can be driven by sunlight using TiO_2 -containing photocatalyst, making the remediation process a zero-cost of energy and resulting in considerable economic savings.

3.3 The problem of oil coagulation in aqueous environment and adsorption of oil droplets over TiO_2

Because of surface tension of oil droplets on the surface of water, it hardly makes oil droplets lay flatter instead ball up. This could cancel the solar irradiation to get into micro-crevices of the oil droplets even better, which in turn can result in promptness to sluggish photoremediation process. Besides, ball up formation as the result of coagulation of oil in aqueous environment could create a kind of blanket that can entrap colloidal particles of TiO_2 -containing photocatalyst and cut bridge for harvesting of light meant to activate the photoremediation process. Therefore, to apply TiO_2 nanocomposite in the remediation of oil spills remediation in surface waters as well as soils and make it of practical significance and attractive for large-scale environmental applications, the TiO_2 -containing material need to be made with surface property that at same time bring about attraction of lay flattered oil droplets and adsorption to the surface of buoyant TiO_2 nanocomposite, for effective solar-driven remediation of spilled oils. Such problem can be eliminated with an organic-based material that has a reduced surface energy, low density, high porosity and adsorption ability as well as good elasticity. For example, organobentonite was sufficiently enough to disturb the surface tension of oil droplets on the surface of water [18], which in other words, can make oil droplets lay flatter instead to ball up. Consequently, TiO_2 -containing nanocomposite that is architecturally constructed with superhydrophobicity and superoleophilicity can selectively and smartly facilitate controllable separation of oil from oil/water mixtures and subsequently photoremediate adsorbed oil over the material.

The architectural design of porosity of buoyant TiO_2 nanocomposite cannot only increase the specific surface area but also provide a number of adsorption sites and paths for oils to be in retention in the material. The pore design can primarily decrease the density of the material and enable it easy to enclose oils for rapid degradation and mineralisation. For example, graphene nanosheet can be anchored into the in the architectural framework of TiO_2 nanocomposite to generate micro-pore, meso-pore and macro-pore structures, as it was reported that it provided abundant adsorption sites for oils and organic [80–83]. For recycling and avoidance of damage, when C-C bonds are architecturally cross-linked in the framework of TiO_2 nanocomposite the carbon based architecture of the material can perfectly remain in its original composition and framework. Hence, a combination of adsorption with photochemical remediation of spilled oils through the utilisation of solar energy over TiO_2 -based structural framework is another elegant route that can directly decompose spilled oil into inorganics without any further procedural treatment and thus, could be highly promising for practical applications in both surface waters and soils.

3.4 The oil-TiO₂ nanocomposite binding strength in turbulent flow

Turbulent motions due to strong tide and wind in surface water and soil environments can disturb oil-TiO₂ nanocomposite binding strength and stability. These turbulent motions can produce an external breaking force that destroys binding between two bodies. The binding strength can be related to the inter-particle bonds between aggregate components which involves surface interaction between oil and TiO₂ nanocomposite. Therefore, an oil-TiO₂ nanocomposite binding force will be broken when the shear force applied to their surface of contact is larger than the bonding strength within the cohesion. As such, it is important to architecturally design TiO₂-containing nanocomposite with capacity to resist shear force in a situation of turbulent condition be it in water or soil environment. This will play an important role in determining performance and general acceptance of TiO₂-containing nanocomposite in real oil spill remediation application. The strength of surface interaction between oil and TiO₂-containing nanocomposite will be controlled by two counteracting forces under a given turbulent condition, namely, the oil-TiO₂-containing nanocomposite binding force and the turbulent breaking force of the fluid-material surface contact. The binding force is related to the material's morphological characteristics, and the breakage of binding is to be governed by turbulence kinetic parameters [84]. In this part, the oil-material's binding force and the turbulent breaking force of fluid can be deduced from morphological characteristics of material and the force of attraction between oil and the material under application. However, a method for quantitative evaluating the strength of oil-material's binding force can also be developed based on the binding and the breaking forces of the surface contact between oil and TiO₂-containing nanocomposite. For easy comprehension, under a given turbulent condition, it will be deduced that the critical condition of the breakage of surface interaction between oil and TiO₂-containing nanocomposite is considered to be the binding force equal to the breaking force, which can be written in the following form.

$$B_f = F \quad (6)$$

When TiO₂-containing nanocomposite is architecturally designed with given pore size, an increase in effective adsorption that bring spilled oils much closer to the material can facilitate an increase in oil density that would be larger enough to be stored in the macropores of the nanocomposites. This in effect can result in enhancement of adherence of the oils to the TiO₂-containing nanocomposites, which is beneficial for the improvement in oil retention capacity of the material that can allow adsorbed oil to resist turbulent motion either cause by tide or wind in water or soil environment. In addition, in response on the problem of turbulent motion particularly in surface water environment, TiO₂-containing nanocomposite can be engineered to a strong magnetic response to an external magnetic field according to the magnetization curve. In effect, it is expected that an architecturally designed TiO₂-containing nanocomposite can be easily controlled by an external magnetic field, and then oils can be made to be strongly attracted to the magnetic component of the nanocomposite with which the adsorbed oils are to be retained structural stable. This can provide high contacting rate between spilled oils and the material as well as additional kinetic energy that could enhance the overall degradation and mineralisation rate of spilled oils in surface waters and soils. Hence, removal of spilled oils from the surface of ocean and soil environments can also be achieved in large scale through strategic TiO₂ photoremediation process.

4. Conclusion

The problem of oil spill accidents unto aquatic and terrestrial environments remains one of the series of severe environmental and ecological damages on mother Earth planet, which when not properly managed causes long-term great distortion of ecological equilibrium that consumes lots of financial and bio-diversified resources. To address this kind of environmental issue with vigour considering the problem of complexity of oil spill strongly interested to be managed within the shortest possible treatment time through use of renewable and cost-free energy source for just to maintain ecological equilibrium, development of solar-driven oil spill remediating material with highly desired self-multifaceted features and functions is unwaveringly needed.

Amongst the remediation technology which would completely remove spilled oils from surface waters and soils with cost-free energy, TiO_2 photocatalysis has a proven potential to treat “difficult-to-remove” spilled oils inexpensively and thus, is expected to play an important role in large-scale oil spill remediation challenges. Despite the substantial progress made in TiO_2 photocatalysis, considerable opportunities and commercialisation-related challenges still remain in oil spill remediation using TiO_2 . This clearly demonstrates that gaps exist between material research and application studies for practical application of TiO_2 -containing nanocomposite in oil spill remediation. However, as the complexities and hindrances involved in oil spill remediation using TiO_2 photocatalysis can be modelled to overcome the limitations, such provides the ground basis for designing better TiO_2 -containing nanocomposite for utilisation of full spectrum of solar radiation that is adequate to meet the demands of large-scale commercial use of TiO_2 in oil spill remediation. It is expected that this fundamental understanding of remedies to overcome TiO_2 limitations in oil spill remediation dispels the fear of whether or not modified- TiO_2 can perform well and therefore, it needs to be considered for incorporation within commercial oil spill remediation products over the coming years.

List of Nomenclature

C-C	carbo-carbon bond
CO_2	carbon dioxide
H_2O	water
NIR	natural infrared
OH^\bullet	hydroxyl radical
$\text{O}_2^{\bullet-}$	super peroxide oxygen radical
pH	potential of hydrogen (in a scale used to specify acidity or basicity of an aqueous solution)
RE	rare earth
TiO_2	titanium dioxide
UV	ultraviolet

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